POLYMERIC SCHIFF BASES. XVI. ALTERNATE SYNTHESES FOR THE IMINOBENZYLIDENE POLYMERS

G. F. D'Alelio, F. R. Meyers*, W. F. Strazik** and R. L. Germonprez***
Department of Chemistry, University of Notre Dame Notre Dame, Indiana 46556

ABSTRACT

Eight monomers, considered as suitable for the direct synthesis of iminobenzylidene polymers, $\{NC_6H_4CH_{\overline{1n}}\}$, which pass through a tractable, fusible stage, have been synthesized. The polymerization of four of these monomers yielded insoluble, infusible brick-dust polymers. With the exception of p-CH₃CONHC₆H₄CHO and p-C₆H₅CH=NC₆H₅CH=NC₆H₅ little advantage accrues to the use of these new monomers in the synthesis of the desired polymers, which appear to be best prepared by polymerizing the trimers of m- and p-aminobenzaldehyde in solution of benzylideneaniline.



ff 653 July 65

*NASA Postdoctoral Fellow, University of Notre Dame, 1968.

**Xerox Corporation Fellow, University of Notre Dame, 1966-1968.

***NDEA Fellow, University of Notre Dame, 1967--.

N 68-32189 (THRU)

FACILITY FORM 602

INTRODUCTION

The direct synthesis (equation 1), of high molecular weight, black poly-to-iminobenzylidene], H_2 = NC_6H_4 CH=0, from o-aminobenzaldehyde was reported in a previous publication (1);

n o-H₂NC₆H₄CHO
$$\rightarrow$$
 H₂ \neq NC₆H₄CH \neq nO + (n-1) H₂O (eq. 1)
The direct synthesis of the analogous meta- and para-polymers was not accomplished because the methods used (1) to synthesize the monomeric meta- and

para-aminobenzaldehydes from the nitrobenzaldehydes by catalytic or stannous chloride reductions yielded instead, yellow brick-dust trimers. The formation of trimers is attributable to the acidic medium which catalyzed the self-condensation of the aminoaldehyde. The black meta- and para-polymers were prepared (1) by polycondensation in benzylideneaniline (equation 2) which was shown to be equivalent to a bis-Schiff base exchange reaction (2,3).

The synthesis of crude para-aminobenzaldehyde in an alkaline medium by the reaction of p-nitrotoluene with an aqueous mixture of sodium polysulfide, flowers of sulfur and sodium hydroxide has been reported (4). The yields are relatively low and the product may contain low molecular weight polymers as impurities. Attempts at recrystallization from many solvents and even from water, lead to further polycondensation and a product of broad melting point range is obtained (4). In an extension of the previous studies (1), we observed that the rapid heating of p-aminobenzaldehyde at 170-180°C in nitrogen yielded orange-colored, intractable brick-dust polymers. Accordingly, it appeared desirable to investigate other syntheses of the polyiminobenzylidenes from other reagents, some of which might be relatively more stable as monomers than the aminobenzaldehydes.

This paper reports some new monomers synthesized for this purpose, the results of the polymerization of these monomers, and a comparison of the properties of these polymers with those of the polymers previously prepared (1) from the trimers by equation 2.

The monomers selected for this study are A-B type monomers (1) in which the chemical nature of the reactive groups corresponds to those previously studied (2) in the reactions of the A-A with the B-B type monomers. Thus, the polymerizations of these A-B monomers can be similarly classified (1) as amine-exchange, bis-exchange, etc., as shown in equations 3 to 10 inclusive:

1. Amine Exchange (2)

$$n H_2NC_6H_4CH=NC_6H_5 \rightarrow H_2N_4NC_6H_4CH=NC_6H_5 + (n-1) C_6H_5NH_2$$
 (eq. 3)

2. Aldehyde Exchange (2)

$$n C_6 H_5 CH = NC_6 H_4 CHO \rightarrow C_6 H_5 CH = NC_6 H_4 CH = 0 + (n-1) C_6 H_5 CHO$$
 (eq. 4)

3. Bis Exchange (2)

$$n C_6H_5CH=NC_6H_4CH=NC_6H_5 \rightarrow C_6H_5CH=NC_6H_4CH=NC_6H_5 +$$

$$(n-1) C_6H_5CH=NC_6H_5 \qquad (eq. 5)$$

4. Aldehyde-Amide Exchange (5,6)

$$n CH_3CONHC_6H_4CHO \rightarrow CH_3COOH CH_3COOH CH_3COOH (eq. 6)$$

5. Acetal-Amide Exchange (5,6)

n
$$CH_3CONHC_6H_4CH(OC_4H_9)_2 \rightarrow CH_3CO \longrightarrow NC_6H_4CH \longrightarrow (OC_4H_9)_2 + (n-1) C_4H_9OH + (n-1) CH_3COOC_4H_9$$
 (eq. 7)

6. Acetal-Schiff Base Exchange (5,6)

$$n C_6H_5CH=NC_6H_4CH(OC_4H_9)_2 \rightarrow C_6H_5 \neq NC_6H_4CH \neq n (OC_4H_9)_2 +$$

$$(n-1) C_6H_5CH(OC_4H_9)_2 \qquad (eq. 8)$$

7. Schiff Base-Amide Exchange (5,6)

8. Amine-Acetal Exchange (5,6)

$$n p-H_2NC_6H_4CH(OC_4H_9)_2 \rightarrow H_2 + (OC_4H_9)_2 +$$

$$2 (n-1) C_4H_9OH$$
(eq. 10)

The polymerization reactions of equations 3 to 10 would be contingent, of course, on the successful syntheses of the required monomers.

EXPERIMENTAL

Monomers

- a) p-Aminobenzaldehyde (I), m.p. 69-71°C, was prepared in a 54% yield by the procedure published in Organic Syntheses (4).
- b) p-Formylacetanilide, p-CH₃CONHC₆H₄CHO, (II), was purchased from Eastman Kodak Chemicals, recrystallized from absolute ethanol, and dried in a vacuum oven; m.p. 149-153°C. Its infrared spectrum is shown in Figure 1.
- c) p-Acetamidobenzylidenedibutyl ether, p-CH₃CONHC₆H₄CH(OC₄H₉)₂. Attempts to synthesize this monomer from (II) and butyl alcohol, using p-toluenesulfonic acid catalysis by the continuous benzene-azeotropic method previously reported (5,6) for the synthesis of p-xylylidenetetrabutyl ether, yielded a brick-dust product, m.p. > 300°C, which was insoluble in dimethylacetamide and whose infrared spectrum showed a low concentration of the acetal function. The elemental analysis for carbon, hydrogen and nitrogen yielded values which indicated the product was an oligomer.

Analysis: Calc'd for C₁₇H₂₇NO₃: C, 69.62; H, 9.22; N, 4.77.

Calc'd for C₃₈H₄₂N₄O₃: C, 75.72; H, 7.02; N, 9.29.

Found: C, 77.16; H, 8.04; N, 8.32.

d) p-Acetamidobenzylideneaniline, p-CH₃CONHC₆H₄CH=NC₆H₅, (III), was prepared from (I) and aniline by the continuous azeotrope method previously reported (7), m.p. 140-141°C. Its infrared spectrum is shown in Figure 2.

<u>Analysis</u>: Calc'd for C₁₅H₁₄N₂0 : C, 75.61; H, 5.92; N, 11.76. Found : C, 74.93; H, 5.87; N, 11.78.

e) p-Nitrobenzylidenedibutyl ether, p-0₂NC₆H₄CH(OC₄H₉)₂, was prepared from p-nitrobenzaldehyde and butyl alcohol using p-toluenesulfonic acid catalysis by the continuous azeotropic method previously reported (5,6), b. p. $\frac{25}{146} = 1.4953$. Its infrared spectrum is given in Figure 3.

Analysis: Calc'd for $C_{15}H_{23}NO_4$: C, 64.04; H, 8.24; N, 4.98. Found: C, 64.13; H, 8.19; N, 4.96.

f) p-Aminobenzylidenedibuty1 ether, p-H₂NC₆H₄CH(OC₄H₉)₂, (IV). Attempts to synthesize (IV) by the catalytic hydrogenation (5% palladium-on-charcoal) of p-nitrobenzylidenedibuty1 ether in benzene or dioxane at room temperature by procedures reported previously for the reduction of yielded nitroacetophenones (1), / 60% of the product as infusible polymer (m.p. $> 300^{\circ}$ C) and 40% as an oily product, $n_{\rm D}^{25} = 1.5235$ which was glassy when cooled to 0°C; its infrared spectrum is shown in Figure 4., and its elemental analysis indicated it was a mixture of monomer and dimer.

<u>Analysis</u>: Calc'd for C₁₅H₂₅NO₂: C, 71.67; H, 10.02; N, 5.57. Found (for oil): C, 72.55; H, 9.27; N, 6.89.

g) p-Aminobenzylideneaniline, p-H₂NC₆H₄CH=NC₆H₅, (V), was prepared by the method given by Rossi (8), from aniline and freshly prepared p-amino-benzaldehyde (I), m.p. 110-115°C, accompanied by polymerization. Its infrared spectrum is given in Figure 5.

Analysis: Calc'd for C₁₃H₁₂N₂: C, 79.56; H, 6.16; N, 14.27. Found: C, 79.77; H, 6.08; N, 14.11. h) p-Formylbenzylideneaniline, C₆H₅CH=NC₆H₄CHO, (VI), was prepared from freshly prepared p-aminobenzaldehyde (4) and freshly distilled benzaldehyde by the method given by Rossi (8) for (V); on heating it showed decomposition and melting in the range of 100-120°C. Its infrared spectrum is shown in Figure 6.

<u>Analysis</u>: Calc'd for C₁₄H₁₁NO: C, 80.36; H, 5.30; N, 6.69.

Found: C, 80.28; H, 5.33; N, 6.72.

i) p-Benzylideneiminobenzylidenedibutyl ether, p-C₆H₅CH=NC₆H₄CH(OC₄H₉)₂, (VII). The reaction of (IV) with benzaldehyde in benzene by the continuous azeotropic method (7), yielded a mixture of dimers and trimers which were fusible, having a broad softening range of 130-145°C, and whose infrared spectrum, shown in Figure 7, is more representative of an oligomer than of a monomer, and in which the bands for the acetal moieties are absent.

<u>Analysis:</u> Calc'd for C₂₂H₂₉NO₂: C, 77.84; H, 8.61; N, 4.13.

Found: C, 79.71; H, 7.15; N, 7.02.

j) p-Benzylideneiminobenzylideneaniline, p-C₆H₅CH=NC₆H₄CH=NC₆H₅, (VIII), was prepared by the continuous azeotropic method (7) from (a) benzaldehyde with (V), and (b) from aniline with (VI). Its infrared spectrum is shown in Figure 8, m.p. 85°C.

<u>Analysis</u>: Calc'd for $C_{20}H_{16}N_2$: C, 84.47; H, 5.67; N, 9.85.

Found: C, 84.51; H, 5.67; N, 9.79.

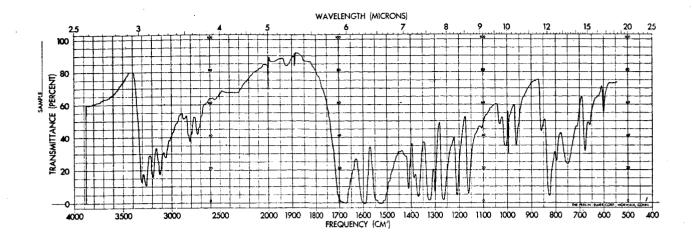


Figure 1. Infrared Spectrum of p-CH₃CONHC₆H₄CHO, (II), KBr disc.

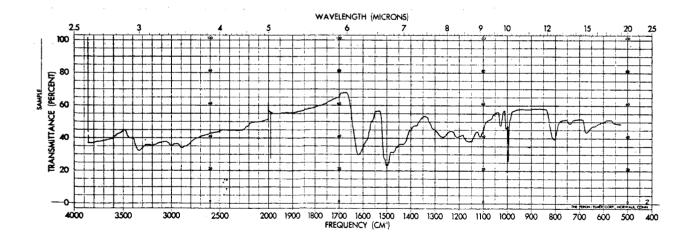


Figure 2. Infrared Spectrum of p-CH₃CONHC₆H₄CH=NC₆H₅, (III), KBr disc.

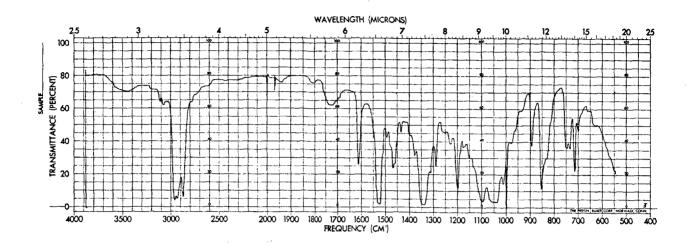


Figure 3. Infrared Spectrum of p-0₂NC₆H₄CH(OC₄H₉)₂, KBr disc.

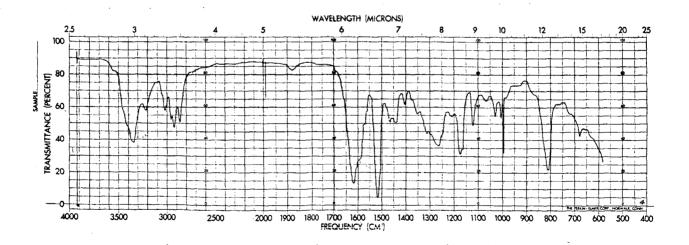


Figure 4. Infrared Spectrum of p-H₂NC₆H₄CH(OC₄H₉)₂, (IV), KBr disc.

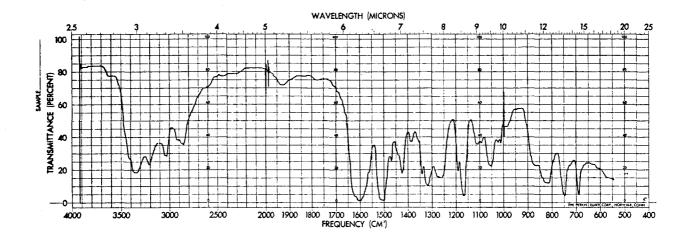


Figure 5. Infrared Spectrum of p-H₂NC₆H₄CH=NC₆H₅, (V), KBr disc.

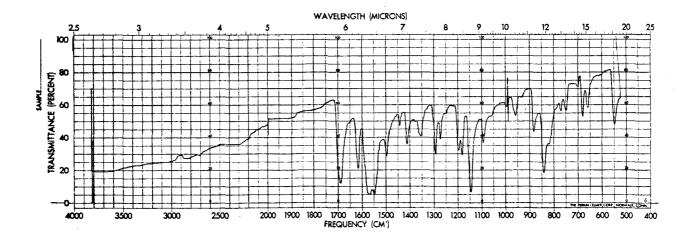


Figure 6. Infrared Spectrum of $C_6H_5CH=NC_6H_4CHO$, (VI), KBr disc.

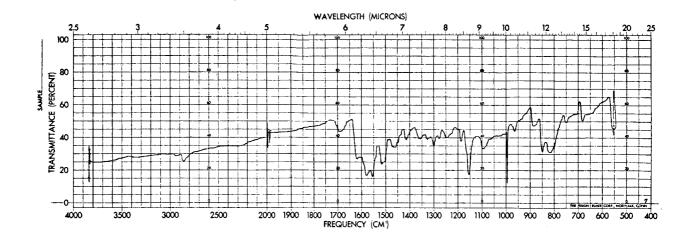


Figure 7. Infrared Spectrum of p-C₆H₅CH=NC₆H₄CH(OC₄H₉)₂, (VII), KBr disc.

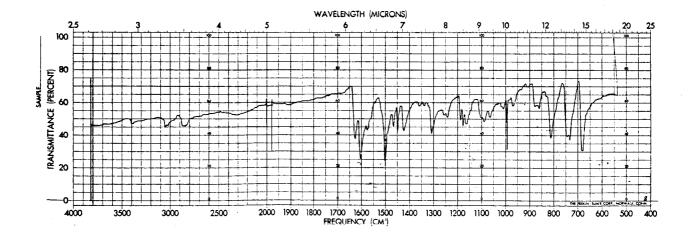


Figure 8. Infrared Spectrum of p-C₆H₅CH=NC₆H₄CH=NC₆H₅, (VIII), KBr disc.

Polymerizations.

The polymers were prepared by the melt polymerization technique under an inert atmosphere using procedures previously published (1,2). The polymerization cycle was

Temperature	Time (hours)
180°C	1
225°C	2
325°C	8

The polymerizations were attempted first as uncatalyzed reactions; when readily polymerization did not occur/under these conditions, the reactions were repeated using 0.5-weight-% of zinc chloride as the catalyst. The infrared spectra of the polymers were recorded as KBr discs (1). In accordance with previous coding (1,2), these products are designated as H325 polymers. The relevant data is given in Table 1.

Postheating of Polymers at 400°C.

Portions of some of the H325°C polymers were postheated (2) under nitrogen at 400°C for four hours, and the yields are given in Table 1. In accordance with previous coding (1,2), these products are designated as the H400 polymers.

Table 1

Some Relevant Data on the H325 and H400 Polymers

								1		
H400 Polymer % Yield		* * * * * * * * * * * * * * * * * * *	62.6	73.4	-		1 2 1 2	88.6	91.2 101.1	
ıt	2	4	12.81	13.08	13.21	1 1	1 1 1		12.12	9.49
Analysis Per Cent	Þ	đ	5.17	4.59	4.52	1 1 1	# # #	-	4.51	5.37
Analys	ر	>	77.16	81.63	81.74		# 1 1	* * * * * * * * * * * * * * * * * * * *	81.88	85.34 85.62
%	% Yield		0.66	73.1*	82.6	102.0	101.7	102.4	97.2	96.1 108.7
Observations	Observations		no melt; yellow brick dust polymer	fusible melt; dark brown, glassy button	fusible melt, light brown glassy button	dark orange, brick dust, infusible	yellow, brick dust, infusible	orange brown, brick dust, infusible	fusible melt, dark brown, glassy button	fusible melt, brown- black, glassy button
	CHH B	В	0=	9	=NC ₆ H ₅	-0C4H9	=NC ₆ H ₅	0=	-0C4H9	=NC ₆ H ₅
	ZnC12 A #NC6H4CH4 B	A	H-	н- сн ₃ со-	н- сн ₃ со-	H- H-	-H -H	C ₆ H ₅ CH=	C6H5CH=	C ₆ H ₅ CH=
	ZnC12		Ou	no	yes	ou	ou	yes	yes	no yes
	Monomer		Н	II	III	** \(\bar{1}\)	Λ	VI	***IIA	VIII

* Part of monomer sublimed during reaction. ** Fusible monomer-dimer mixture. *** Oligomeric and fusible.

Thermogravimetric Analyses.

The procedure previously published was used in the thermoanalyses of the polymers (1,2). Only those polymers which passed through a fusible stage were evaluated; the brick-dust polymers were not tested. The thermogravimetric data for the H400 polymers are summarized in Table 2.

Table 2

Thermogravimetric Data in Nitrogen for the H400 Polymers

Polymer	Per Cent Weight Loss at °C								
Tolymer	400	500	600	700	800	900	1000	1176	
II	0.0	0.0	2.7	5.0	8.2	13.1	14.8	15.8	
III	0.0	0.0	2.8	5.2	8.4	14.0	15.1	18.1	
AII	0.0	0.0	3.6	5.4	8.6	14.4	15.3	18.4	
VIII	0.0	0.0	1.7	5.1	8.3	13.6	14.6	17.3	

DISCUSSION AND CONCLUSIONS

Monomers

Since the polymerization tendency of the m- and p-aminobenzaldehydes, prepared by the reduction of the corresponding nitro-aldehydes, were substantially identical (1), the present study was limited only to the para substituted monomers. In this study, crude monomeric p-aminobenzaldehyde (I), m.p. 69-71°C, was prepared (4) in a 54% yield from p-nitrotoluene. The high tendency to self-condensation was evident when recrystallizations were attempted from numerous solvents, including benzene, ethanol, dioxane and water. In solution, trimeric products formed readily, thereby increasing and broadening the melting point range of the product. When refluxed in the solvent, infusible oligomeric products, m.p. > 300°C, were obtained. When held at its melting point of 69-71°C, (I) was converted to a yellow, oligomeric brick-dust.

The polymerization tendency of (I) was reduced somewhat when its -NH₂ or -GHO group or both groups were converted to appropriate derivatives. The p-formylacetanilide (II) was much more stable than (I) and it showed only a slight tendency to polymerize at its melting point. However, attempts to convert (II) to the dibutyl acetal by the acid catalyzed reaction with butyl alcohol by the continuous benzene-azeotropic method found effective for other aromatic aldehydes yielded insoluble, infusible polymeric products by the elimination of acetic acid in the form of butyl acetate. However, the uncatalyzed reaction of (II) with aniline by the continuous azeotropic procedure yielded easily the corresponding benzylideneaniline derivative (III). Monomer (III) showed little tendency to polymerize at its melting point.

Numerous attempts to produce the dibutyl acetal (IV) directly from (I) were unsuccessful; partial success of the synthesis of (IV) was achieved by

the catalytic reduction of p-nitrobenzylidenedibutyl ether, yielding a mixture of brick-dust-oligomers and an oil whose analysis indicated that it was a mixture of monomer and dimer; this oil was used directly since attempts to isolate the monomer from the mixture yielded further amounts of polymer.

Monomer (V) was prepared by the method of Rossi (8) from freshly prepared (I) and a large excess of aniline (1:10 mole) by heating the mixture to the boiling point of aniline followed by cooling in an ice-water mixture, separating the precipitate, and washing it with a 50:50 mixture of hexane-diethyl ether. Prolonged heating of the reaction mixture at the boiling point of aniline precipitated brick-dust polymers. At its melting point (V) polymerized readily.

Monomer (VI) was prepared from (I) and benzaldehyde by the same procedure used to prepare (V); a nitrogen atmosphere was used to avoid oxidation of the benzaldehyde; on heating, (VI) polymerized in the range of 100-120°C.

The uncatalyzed reaction of (IV) with benzaldehyde did not yield the monomeric benzylidene derivative (VII) but gave an oligomeric product which was fusible with a broad softening range of 130-145°C; when held at 145°C the oligomers polymerized further. Monomer (VIII) was the most stable of the monomers prepared and it showed little or no tendency to polymerize at its melting point.

POLYMERIZATIONS

Monomers (IV), (V) and (VI) polymerized to infusible, low molecular weight brick-dusts varying in color from yellow to orange, and in this respect were similar to (I). However, monomers (I), (IV), (V) and (VI) and the resulting brick-dust polymers, as well as the trimer of p-acetamidobenzylidenedibutyl ether could be polymerized in solution in benzylideneaniline (1), but since the purpose of this study was to evaluate new monomers which would yield fusible, tractable, black polymers directly on polymerization, they were not investigated further.

The uncatalyzed polymerization of (II) yielded acetic acid as shown in equation 6, and during the course of its polymerization considerable amounts of monomer sublimed from the reaction mass causing a reduction in the yield of polymer. However, since this is an A-B type polymerization, the critical stoichiometry is not disturbed by the lost of A-B monomer. The polymerization was well moderated and the viscosity of the melt increased as the color changed progressively from light to dark brown to a hard, brown-black glassy button. The polymerization was highly accelerated by the addition of catalytic quantities of Lewis acid; the addition of 0.25% weight per cent of zinc chloride to the monomer increased the yield to 94%. This polymerization of the A-B monomer (II) differs markedly with the comparable unsuccessful A-A plus B-B monomer reaction (6) of p-CH3CONHC6H4NHOCCH3 + p-OHCC6H4CHO, which yielded insoluble intractable, infusible polymer products with little or no evidence for the presence of a C=N structure in the polymers; even though the monomeric prototype reactions yielded Schiff bases (6). It is believed that the intractability of the condensation product prevented the elimination of the acetic acid. this case of the A-B type monomer, the polymer, as it is formed, was soluble in unconverted (II) which maintained the mixture as a melt and allowed the reaction to proceed to completion. This belief was confirmed, to some measure, by dissolving p-aminobenzaldehyde trimer, H2+NC6H4CH+30 in (II) and polymerizing the solution to/tractable, fusible polymer (9).

The uncatalyzed polymerization of (III), shown as equation 9, was very sluggish and accordingly, zinc chloride was used as a catalyst. Its polymerization paralleled that of (II), eliminating acetanilide instead of acetic acid. In this polymerization, the A-B type monomer solubilized the polymer as it was formed and allowed the reaction to proceed to a higher degree of condensation; thus, it also differs with the related unsuccessful A-A with B-B monomer type of polymerization (6) of p-CH₃CONHC₆H₄NHOCCH₃ with p-C₆H₅CH=NC₆H₄N=HCC₆H₅.

The polymerization of the fusible oligomers of (VII), used instead of the monomer shown in equation 8, was sluggish and required zinc chloride catalysis; it yielded a dark-brown polymer rather than brownish-black product and in this respect is similar to the acetal-Schiff base exchange of the A-A plus B-B polymerization (6) of $p-C_6H_5CH=NC_6H_4N=CHC_6H_5$ with $p-(BuO)_2HCC_6H_4CH(OBu)_2$ which proceeded best (6) in the presence of benzylideneaniline.

The polymerization of (VIII) by the Schiff base exchange reaction of equation 5 proceeded as a well moderated, uncatalyzed or catalyzed reaction to yield a product which was equivalent to the product obtained by the polymerization of the trimer of p-aminobenzaldehyde in benzylideneaniline (1). The zinc chloride catalyzed reaction produced a higher yield of polymer at 325°C and 400°C than the uncatalyzed reaction; both the catalyzed and uncatalyzed reactions produced higher yields of polymer than the other reactions which did not eliminate benzylideneaniline. This is in agreement with previous findings (10-12) which indicated not only that the benzylideneaniline is retained tenaciously by the polymer, but, that it may also undergo reaction with the polymer.

The infrared spectra of all the brown or black H325 and H400 polymers of this study were substantially identical to those published (1) for the aminobenzaldehyde trimers polymerized in benzylideneaniline. Similarly, the thermogravimetric data for the brown to black H325 and H400 polymers of this study were substantially identical to those published for the polymeric azomethines prepared from aminoarylcarbonyl monomers (1).

The present study indicated that, because of their instability, most of the new monomers synthesized, including p-aminobenzaldehyde, were not too suitable for the preparation of the polymers. The exceptions to this generalization were, the formylacetanilide (II), and its Schiff-base derivative (III) and the bis-Schiff base (VIII). Monomer (III), which eliminated acetanilide, offered little or no advantage over (II), which eliminated acetic

acid, since acetic acid is eliminated more readily than acetanilide. In addition, (III) is synthesized from (II), adding an additional step to the process for which no advantage is gained. Monomer (II) is derived by acetylation of (I); this additional step contributes an advantage in that a tractable, fusible intermediate polymer can be obtained from the direct polymerization of (II) and not of (I) without the expediency of adding benzylideneaniline as a solvent. The stability of monomer (VIII) is about the same as (II) and polymerizes readily to satisfactory polymers. However, the polymer product is identical to that obtained by the polymerization of aminobenzaldehyde polymers in benzylideneaniline, and the complications of the synthesis of (VIII) does not particularly warrant its preparation to achieve a result which can be obtained rather simply by the use of the trimer in benzylideneaniline.

Though a number of new syntheses for the iminobenzylidene polymers has been achieved, it may be concluded that the choice syntheses are those from (a) p-formylacetanilide (II) and (b) the aminobenzaldehyde trimers dissolved in benzylideneaniline.

NGL-15-004-001 (NSG-339)

Acknowledgment. The work was performed under NASA Grants-NsG339 and NGR-15-004-028. The generous contribution of time and effort by W. F. Strazik and R. L. Germonprez is also gratefully acknowledged.

REFERENCES

- G.F. D'Alelio, W.F. Strazik and T.F. Huemmer, Polymeric Schiff Bases.
 X., J. Macromol. Sci.-Chem., in press.
- G.F. D'Alelio, J.V. Crivello, R.K. Schoenig and T.F. Huemmer, J. Macromol. Sci.-Chem., A-1(7), 1161 (1967).
- G.F. D'Alelio, J.V. Crivello, R.K. Schoenig and T.F. Huemmer, J. Macromol. Sci.-Chem., A-1(7), 1321 (1967).
- 4.E. Campaigne, W.M. Budde and G.F. Schaeffer, in "Organic Syntheses, Collective Volume IV" (N. Rabjohn, ed.), John Wiley and Sons, Inc., New York, N.Y., 1963, p. 33.
- G.F. D'Alelio, T. Kurosaki and R.K. Schoenig, J. Macromol. Sci.-Chem., <u>A-1</u>(7), 1279 (1967).
- 6. G.F. D'Alelio, T. Kurosaki and T. Ostdick, Polymeric Schiff Bases. IX., J. Macromol. Sci.-Chem., in press.
- 7. G.F. D'Alelio, J.V. Crivello, R.K. Schoenig and T.F. Huemmer, J. Macromol. Sci.-Chem., A-1(7), 1251 (1967).
- 8. G. Rossi, Gazz. Chim. Ital., 44 (II), 263 (1916).
- 9. G.F. D'Alelio, W.F. Strazik and D.M. Feigl, Polymeric Schiff Bases. XVII. Azomethine Copolymers, in preparation.
- G.F. D'Alelio, D.M. Feigl, H.E. Kieffer and R.K. Mehta, Polymeric Schiff Bases. XIII., J. Macromol. Sci.-Chem., in press.
- G.F. D'Alelio, R.K. Mehta, D.M. Feigl, H.E. Kieffer and R. L. Germonprez, Polymeric Schiff Bases. XIV., J. Macromol. Sci.-Chem., in press.
- 12. G.F. D'Alelio, H.E. Kieffer, R.L. Germonprez and R.K. Mehta, Polymeric Schiff Bases. XV., J. Macromol. Sci.-Chem., in press.